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Biosorption efficiency of custard apple (*Annona squamosa) bark* towards the removal of metal complex Orange R dye from aqueous solution and textile industry wastewater

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Abstract: *Biosorption of Metal complex Orange R dye by custard apple bark (Annona squamosa) in aqueous solution and textile industry wastewater was investigated. Batch experiments were carried out to determine the effect of pH, particle size, biosorbent dose, contact time and initial dye concentration. Characterization of biosorbent was also done by FTIR and SEM. Biosorption isotherm models were also applied to experimental data. The results showed that the data fitted well for Langmuir isotherm model as well as Fruendlich isotherm. The study proves the effectiveness of Annona squamosa bark for the removal of metal complex dyes from the wastewater.*

Keywords: *Annona squamosa; Biosorption, Isotherm models, Metal complex Orange R*

I. Introduction

Dyes are toxic and trace materials available in wastewater and Azo dyes are of such type. Dyes usually have a complex aromatic molecular structure which makes them more stable and difficult to biodegrade [1].

Azo dyes are widely used to dye various materials such as leather, plastic, textile, food, paper and cosmetics [2,3] .Azo dyes are Synthetic compounds[4]. Overall annual production of azo dyes in the world is estimated to be one million tons. Therefore the use of azo dyes represents a serious problem worldwide [4, 5]. The adverse effect of these dyes has not only been seen on the environment but also these pose a major concern with regard to human health [6]. Along with polluting nature there has been a slow continuous rise of bioaccumulation of the chemicals affecting photosynthetic processes in plants [7], and imbalance of hormones and immunity loss resulting in cancer in human beings[6, 8, 9].

To overcome these effects of synthetic dyes which are used in various industries, removal of their effects is now an issue of concern as a result of which series of methods are followed for the removal of dyes. There are various conventional methods such as chemical coagulation using alum, lime, ferric sulphate [10], oxidation methods using chlorine and ozone [11] biological treatments, floatation [12] and many more. These have a drawback they are expensive, inefficient and bring forth sludge disposal problem [13] hence the industries interest and main approach is towards low cost and effective method which can remove the dyes from the effluent or wastewater and can support to maintain the balance of nature. Hence the approach of processes likes biosorption using low cost agricultural waste favoured by various industries.

The present study mainly focuses on the biosorbent capacity to biosorb the dyes using biosorption technique. The present study investigated the biosorption of Orange R dye from aqueous solution and textile industry wastewater using custard apple (*Annona squamosa)* bark. The effects of pH, particle size, biosorbent dose, contact time and initial dye concentration on biosorption were studied in detail. Langmuir and Fruendlich isotherm models were used to fit the equilibrium data.

II. Material And Methods

2.1 Structure of Orange R

The Metal complex Orange R (OR) dye was obtained from Zese India LTD, Bangalore, Karnataka. Its IUPAC name is 34-[(2-Hydroxy-5-nitro-phenyl)-hydrazono]-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one. The molecular formula is $C_{16}H_{13}N_5O_4$, molecular weight is339.31 [g/mol] and structure of the OR is shown in figure 1.

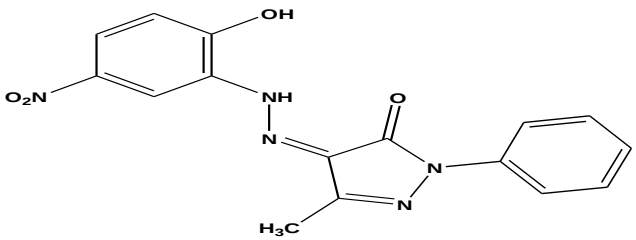


Fig 1- Structure of Orange R

2.2 Dye solution preparation

An accurately weighed quantity of OR dye was dissolved in double distilled water to prepare stock solution (1000mg/L) and further diluted to obtain working solutions of lower concentration 50 mg/L which was determined using the absorbance values before and after the biosorption using UV-Visible Spectrometer(HitachiUV-2910). The pH adjustment of solution was carried out using 0.01N HCl and 0.01N NaOH

2.3 Preparation of biosorbent:

The plant *Annona squamosa* also known as custard apple belongs to the family Annonaceae. The barks of Annona squamosa (ASB) are used in this study. The barks were collected, washed thoroughly and dried in sunlight. Subsequently the seeds were grounded and sieved according to the standards of ASTM (American Society Testing Materials). Biosorbent was washed thoroughly and constantly several times with double distilled water and dried well in sunlight. ASB is stored in a dried and an airtight container for experimental use.

2.4 Characterization of biosorbent

The FTIR and SEM analyses were carried out by (Shimadzu-IRAffinity-1) FTIR Spectrophotometer and ZEISS, (EVO/LS-15).

2.5 Batch experiments

Batch experiments were carried out at room temperature. Different parameters such as, effect of pH ranging from 2.0 to 10.0, particle size ranging from 212µm to 500µm, biosorbent dose ranging from 0.2 g/L to 2.0 g/L, contact time ranging from 10 to 120 min and initial dye concentration ranging from 10 to 50 mg/L were studied. pH adjustment of the solutions were carried out using 0.01N HCl and 0.01N NaOH. Mixtures were taken in 250 mL Erlenmeyer flasks and shaken at 170rpm using mechanical shaker (KEMI KRS 110, India) for a fixed period of time. The mixture was then filtered from ASB and determined spectrophotometrically by recording the absorbance changes at maximum biosorption (490nm) using UV-Vis Spectrometer (HitachiUV-2910). All determinations were done in triplicate average values were considered. Percentage biosorption was calculated by the formula

$$\%Biosorption = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

where C_i and C_f are the initial and final OR concentration (mg/L) respectively

2.6 Physico-chemical characteristics of textile industry wastewater

The wastewater was collected from textile industry located in Bangalore, Karnataka India. The physico-chemical characteristics were determined using standard method of APHA [14]. The results are presented in Table 1.

Table 1: Physico-Chemical Characteristics Of Textile Industry Wastewater

Characteristics	**Contents(mg/L)**
Colour	Yellowish orange
pH	10.69
EC(µs/cm)	2974
TDS	1085
Total hardness	730.9
Calcium	269.3
Magnesium	114.7
Chloride	603.1
Sulphate	338.5
DO	Nil
BOD	1437.2
COD	1926.6

III. Results And Discussion

3.1 FTIR Analysis

Figure 2a and 2b shows FTIR spectra of OR before biosorption on ASB and OR after biosorption on ASB. The bands show the functional groups of sulphur and carboxylic acid and their derivatives. The peak ranging from 544cm^{-1} is due to S-S bonds in figure 2a which are reduced in the figure 2b as observed; this is due to the biosorption of OR on ASB. The peaks between 1539 and above 3740 cm^{-1} indicates N-H bonds and C-N bonds of amine along with overlap C-H stretched bands. The peaks which are reduced in figure2b indicate strong stretching vibration of carboxylic acids groups of amide. An FTIR spectrum of fig 2b shows peaks in low frequency regions and absence of peaks ranging from 514cm^{-1} to 720cm^{-1}because there is a biosorption of OR

on ASB surface, biosorption showed that carbon, hydrogen and atom bonds played major role. Decreased intensity of sharp peaks concluded that OR has been functionalized by ASB.

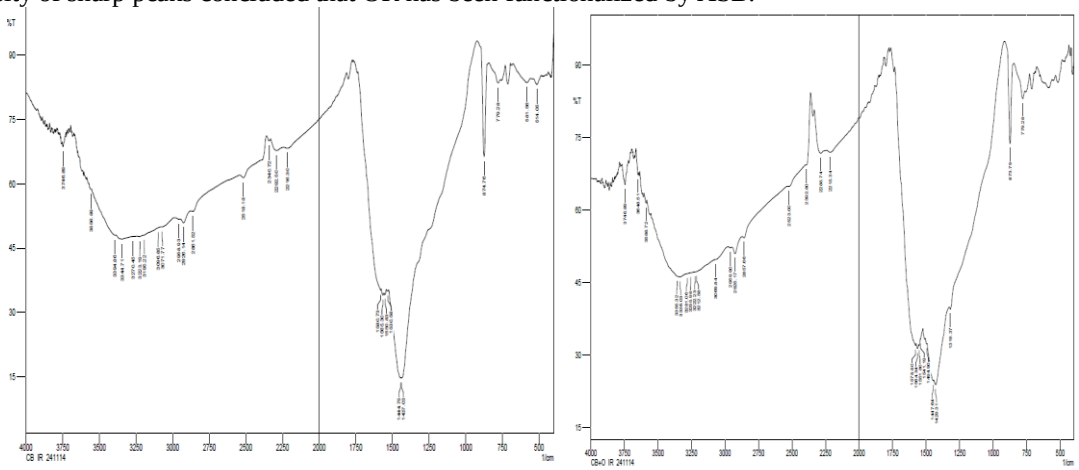


Fig-2 a. FTIR of ASB before biosorption **b. FTIR of ASB after biosorption**

3.2 Scanning Electronic Microscopic Studies (SEM)

The ASB morphology was characterized using SEM and the microphotographs are shown in Figure 3a and 3b.It can be seen that pores within ASB are highly heterogeneous before biosorption of OR which is seen in figure3a. However it is not the case after biosorption since a significant change is observed in the structure of the barks as observed in figure 3b. They appear rougher with the formation of crater-like pores. [15] This phenomenon can be explained by the package of pores involved in dye molecules

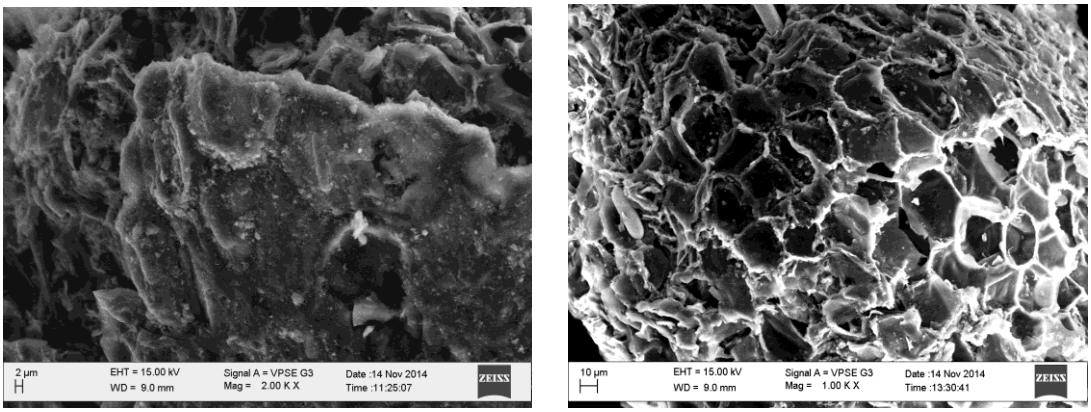
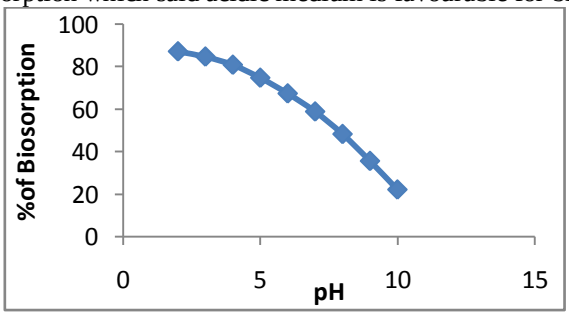


Fig 3a: ASB before biosorption **b: ASB after biosorption**

3.3 Effect of pH

The pH has an important effect on dye biosorption since the pH of the aqueous solution will control the magnitude of the electrostatic charges that are imparted by ionized dye molecules and biosorbent [16, 17].Figure 4 shows the effect of pH on the removal of OR. The highest dye removal efficiency was observed at pH 2.0 where biosorption was 87.06%. The removal percentage then decreased as pH increased from 3 to 10. Similar results were recorded in the other metal complex dyes like acid black 172 and remazol navy blue in the process of biosorption which said acidic medium is favourable for biosorption [17, 18].



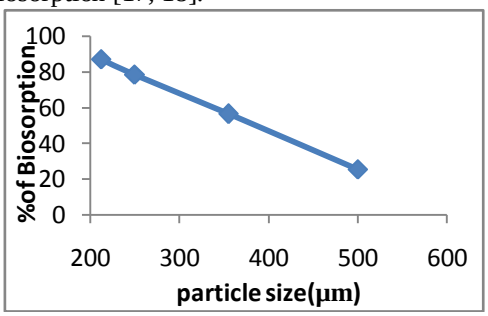


Fig-4 Effect of pH on biosorption of OR by ASB **Fig-5 Effect of particle size on biosorption of OR by ASB**

3.4 Effect of biosorbent particle size

The effects of particle size on the biosorption of the OR on to ASB are shown in the figure 5. The result describes that 87.06% biosorption of OR was achieved at 212µm. As size increased, biosorption decreased by ASB. This clearly defines that decrease in the particle size would increase in the surface area and consequently result in an increase in OR biosorption onto the ASB surface. Various factors are responsible for the low biosorption capacity of OR on the larger particles as they may be over saturation of pore sites or high competition for available sites. Similar kinds of result were recorded [19, 20]

3.5 Effect of biosorbent dose

The biosorbent doses on OR by ASB are shown in figure 6. The results describes that OR biosorption by ASB increases with increase in the biosorbent dose from 0.2 to 0.8 g/L (67.92 to 87.06%).This is due to the increase in surface area which in turn increases the availability of the exchangeable sites on the ASB for the biosorption of OR [21]. Further increase in biosorbent dose beyond 0.8 g/L keeps OR biosorption static which suggest that it has attained equilibrium between the liquid and solid phase. Similar results were observed at >1 g/L and 400 g m^{-3}[22, 23].

3.6 Effect of contact time

The variation of contact time of OR by ASB is shown in figure 7. It was clear that maximum biosorption (87.06%) of OR by ASB was achieved at 90min. A rapid biosorption of the OR by ASB took place at 45min and then the biosorption was slow till it reached the equilibrium. The reason being that, at initial stage there was a more vacant biosorption site which gets occupied later, resulting in the slow biosorption and once the biosorption reaches equilibrium, the contact time and the percentage of biosorption becomes constant.[17,24, 25] .

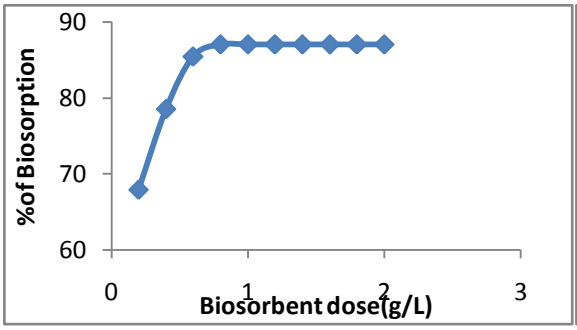


Fig6: Effect of Biosorbent dose on ASB

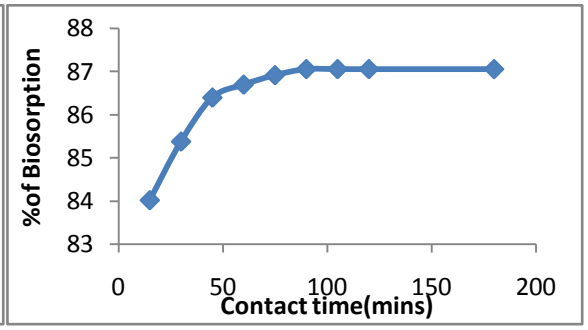


Fig-7 Effect of contact time on biosorption on ASB

3.7 Kinetic isotherms

The Lagergren's pseudo-first-order model and Ho's pseudo-second-order model [26] have been widely used to predict biosorption kinetics. The pseudo-first order equation is generally applicable to the initial stage of the biosorption processes whereas the pseudo-second order equation predicts the behavior over the whole range of biosorption. These two models were used to fit the experimental data of this study whose equations are described in equation (2) and (3)

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \qquad (2)$$

$$\frac{t}{qt} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \qquad (3)$$

where k_1 (min^{-1})is the rate constant of pseudo-first- order adsorption and k_2(g mg^{-1} min^{-1}) is the rate constant of pseudo –second-order adsorption. q_e, amount of dye biosorbed on biosorbent at equilibrium.

Plots of pseudo-first-order and second order are shown in Figure 8 and 9.Results show that pseudo-first-order rate constant (K_1) for OR biosorption by ASB was 2.05X10^{-3} min^{-1} but $q_{e\ cal}$ values obtained largely different than that of $q_{e\ exp}$ values which indicated the non applicability of pseudo- first order model, whereas higher pseudo-second order rate constant (K_2) of 6.38 X 10^{-3} g/mg $min^{-1}$was achieved by ASB, which show rapid OR

biosorption by ASB. The $q_{e\ cal}$ values of pseudo- second order are closer to $q_{e\ exp}$ values and higher regression coefficient (R^2) value was obtained reveal better fitting of equilibrium data to pseudo second order model. This confirmed that involvement of chemical biosorption through exchange or sharing of electrons between biosorbent and biosorbate. [27]. Table 2 describes pseudo-first and second- order of OR biosorption.

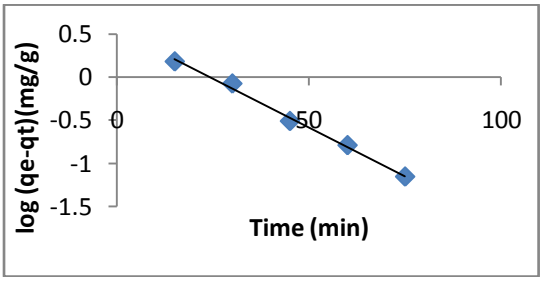


Fig 8:Pseudo-first order for OR by ASB

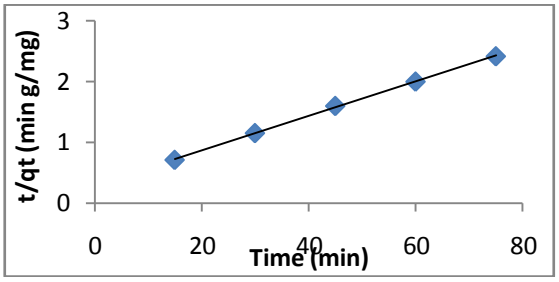


Fig 9: Pseudo-second order for OR by ASB

Table -2 Pseudo First Order And Pseudo Second Order Constants Chosen For Biosorption By ASB

Dye	$q_{e\ exp}$ (mg/g)	Pseudo first order			Pseudo second order		
O.R	34.41	$K_1(min^{-1})$	$q_{e\ cal}$ (mg/g)	R^2	$K_2(g/mg\ min^{-1})$	$q_{e\ cal}$ (mg/g)	R^2
		2.05×10^{-3}	33.26	0.994	6.38×10^{-3}	34.38	0.999

3.8 Effect of initial dye concentration

Figure 10 shows the initial concentration of OR by ASB which describes that the percentage of biosorption decreases (99.60% to 87.06%) with increase in the concentration. This is due to the fact that dye ion concentration causes saturation of biosorption sites on ASB and this blocks further OR biosorption on biosorption sites. As a result of this the biosorption efficiency decreases. [17, 18, 28]

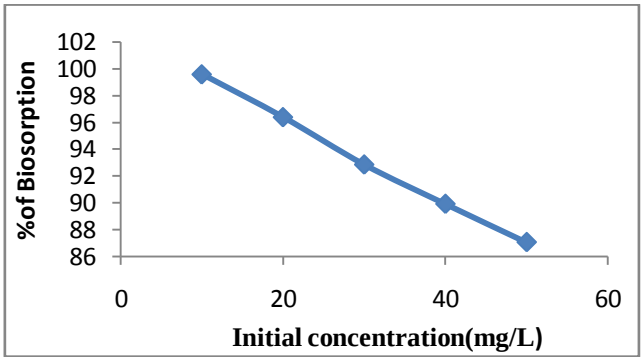


Fig-10 Effect of Initial dye concentration on biosorption of OR by ASB

3.9 Langmuir and Freundlich isotherm

The biosorption data were fitted to two isotherms namely Langmuir and ***Freundlich***. The Langmuir [29] and ***Freundlich*** isotherm [30] model equations are described in equation (2) and (3) respectively.

$$\frac{C_e}{q_e} = \frac{1}{(bq_{max})} + \frac{C_e}{q_{max}} \qquad (2)$$

$$q_e = K_f\ C_e^n \qquad (3)$$

Where, C_e is the equilibrium concentration (mg/L), q_e and q_{max} are the equilibrium and maximum biosorption capacity (mg/g), respectively and b is the Langmuir constant and K_F and n are the Freundlich constant.

Figure 11 shows the linear plot obtained by plotting C_e/q_e versus C_e. The Langmuir model effectively describes the biosorption data R^2 value of 0.999 are given in Table 2. This behaviour indicates a monolayer biosorption. The value of b (162.97 L/g) and Q_{max} (65.10 mg/g) indicates maximum interaction and greater

affinity of OR with ASB [31].Figure 12 shows the linear plot obtained by plotting log q_e versus log C_e. The Freundlich model parameters like R^2 (0.999) values, K_f 15.49 (mg/g) (mg/L) $^{1/n}$ and n (0.83) are given in Table 3. The results indicate that biosorption data for OR fits well to Langmuir model and Fruendlich model. Hence biosorption was monolayer coverage of OR on ASB and the heterogeneity of binding sites on biosorbent surface [17, 28]

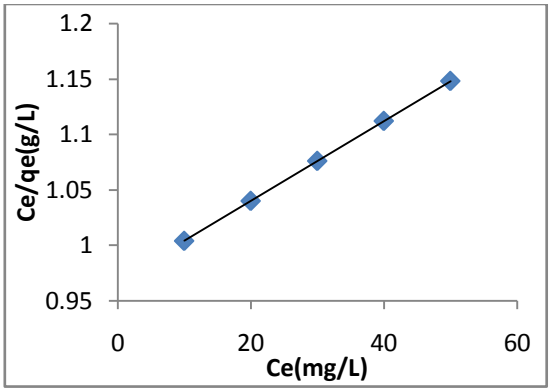


Fig: 11 Langmuir isotherm plot for OR by ASB

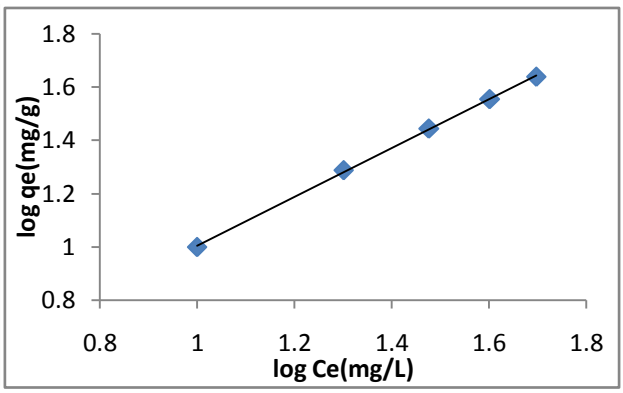


Fig: 12 Freundlich isotherm plot for OR by ASB

3.9 Application of textile industry wastewater

The efficiency of ASB for OR from textile industry wastewater was determined. The experiment was performed in an Erlenmeyer flask containing 50 mL of wastewater sample. To this 212 µm of 0.8 g/L of ASB was added and pH was adjusted to 2.0 using 0.01N HCl and 0.01N NaOH. After 90 min of agitation, the wastewater sample was filtered and the resultant supernatant solution was analysed by UV.Visible spectrophotometer (HitachiUV-2910). Result showed that the OR biosorption from textile industry wastewater was 85.16 % which was less than the aqueous solution. This is due to competition between ions of dyes and co-ions interference for the biosorption sites on the ASB.

Table -3 Langmuir Isotherms and Freundlich Isotherm Parameters for Biosorption By ASB

Dye	Langmuir isotherm			Freundlich isotherm		
OR	Q_{max} (mg/g)	b(L/g)	R^2	K_f(mg/g)(mg/L)$^{1/n}$	n	R^2
	65.10	162.97	0.999	15.49	0.83	0.999

4 Conclusion

The present study investigated the biosorption of OR by ASB from aqueous solution and textile industry wastewater. Characterization of biosorbent clearly shows the porosity and wider surface texture and the FTIR peaks also revealed that biosorption occurred. The biosorption equilibrium was described by the isotherm model. A single-stage batch biosorption system was design for the OR removal which was also outlined based on the isotherm model. Data fitted well for Langmuir model with Q_{max} (65.10 mg/g) as well as Fruendlich model K_f 15.49 (mg/g)(mg/L)$^{1/n}$, proving biosorption was monolayer coverage and the heterogeneity of binding sites on ASB surface for OR. And when the ASB was applied for textile industry wastewater, percentage of biosorption was 85.16% less compared to aqueous solution which was 87.06% due to competition between ions of OR and co-ions interaction of other dyes. It was concluded that the ASB could be used as a promising alternative for OR removal from aqueous solutions and textile industry wastewater.

References

[1]. R. Ansari., A. Mohammd-khah, Z. Mosayebzadeh. "Application of unripe grape juice waste as an efficient low cost biosorbent for dye removal", Annals of Biological Research. (2011),vol. 2, no.5, pp.323-328

[2]. G.S. Gupta, S.P. Shukla, G. Prasad and V.N. Singh, "China clay as an adsorbent for dye house wastewater", Environ. Technol. (1992), 13 pp. 925–936

[3]. Shao, Y. L., Ditmire, T., Tisch, J. W. G., Springate, E., Marangos, J. P., & Hutchinson, M. H. R. Multi-keV electron generation in the interaction of intense laser pulses with Xe clusters. Physical review letters, (1996). 77(16), 3343.

[4]. Stolz, A. Basic and applied aspects in the microbial degradation of azo dyes. Applied microbiology and biotechnology, (2001). 56(1-2), 69-80.

[5]. Pandey, A., Singh, P., & Iyengar, L. Bacterial decolorization and degradation of azo dyes. International Biodeterioration & Biodegradation, (2007). 59(2), 73-84.

[6]. Topaç, F. O., Dindar, E., Uçaroğlu, S., & Başkaya, H. S. Effect of a sulfonated azo dye and sulfanilic acid on nitrogen transformation processes in soil. Journal of hazardous materials, (2009). 170(2), 1006-1013.

[7]. Bayramoğlu, G., Çelik, G., & Arica, M. Y. Biosorption of Reactive Blue 4 dye by native and treated fungus Phanerocheate chrysosporium: Batch and continuous flow system studies. Journal of Hazardous Materials, (2006). 137(3), 1689-1697.

[8]. Lanone, S., Zheng, T., Zhu, Z., Liu, W., Lee, C. G., Ma, B., & Elias, J. A. Overlapping and enzyme-specific contributions of matrix metalloproteinases-9 and-12 in IL-13-induced inflammation and remodeling. (2002).

[9]. Wu, A. H., Yu, M. C., Tseng, C. C., & Pike, M. C. Epidemiology of soy exposures and breast cancer risk. British journal of cancer, (2008). 98(1), 9-14.

[10]. Low, K. S., & Lee, C. K. Quaternized rice husk as sorbent for reactive dyes. Bioresource Technology, (1997). 61(2), 121-125.

[11]. J. H. Churchley, Sci Tech. 1994, 30, 275

[12]. W. J. Weber Jr, "Physico-chemical Methods of Treatment of Water and Wastewater", New York, John Wiley & Sons Inc, 1978

[13]. N. Ahalya and T.V. Ramachandra .Restoration of wetlands - Feasibility Aspects of Biological restoration presented at the National Conference on Aquatic Restoration and Biodiversity – Feb 15-16 2002 in Kongunadu Arts and Science College, Coimbatore, India.

[14]. Clesceri,S.L., Greenberg,A.E., and Eaton,A.D. Standard Methods for the examination of water and wastewater,20th edition, APHA,AWWA and WEF, Washington, DC.,(2012).

[15]. Arami, M., Limaee, N. Y., Mahmoodi, N. M., & Tabrizi, N. S. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. Journal of Colloid and interface Science, (2005). 288(2), 371-376.

[16]. Sponza, D. T., & Işik, M. Decolorization and azo dye degradation by anaerobic/aerobic sequential process. Enzyme and Microbial Technology, (2002). 31(1), 102-110.

[17]. Yang, Y., Lin, X., Wei, B., Zhao, Y., & Wang, J. Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling. International Journal of Environmental Science and Technology, (2014). 11(4), 1093–1100. http://doi.org/10.1007/s13762-013-0306-0

[18]. Ratnamala, G. M., & Brajesh, K. Biosorption of remazol navy blue dye from an aqueous solution using pseudomonas putida. International Journal of Science, Environment and Technology, (2013). 2(1), 80–89.

[19]. Wanna, S., & Pairat, K. Cadmium ion removal using biosorbents derived from fruit peel wastes. (2009).

[20]. Shabudeen P.S.Syed, Study of the Removal of Malachite Green from Aqueous Solution by using Solid Agricultural Waste. Research Journal of Chemical Sciences, (2011). Vol. 1, Available online at: www.isca.in

[21]. Tunc O., Tanacı, H., Aksu, Z.,Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye, Journal of Hazardous Materials, (2009) 163, 187-198

[22]. R.L. Tseng, F.C. Wu and R.S. Juang, Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons, Carbon (2003), 41 pp. 487–495

[23]. Veeramalini, J. B., Sravanakumar, K., & Joshua Amarnath, D. Removal of reactive yellow dye from aqueous solutions by using natural coagulant. Int J Sci Environ Technol, (2012). 1, 56-62.

[24]. Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., & Ranganathan, K. Removal of dyes from aqueous solutions by cellulosic waste orange peel. Bioresource Technology, (1996). 57(1), 37-43.

[25]. Ho, Y. S., & McKay, G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Process Safety and Environmental Protection, (1998). 76(4), 332-340.

[26]. Reddy, M. S., Sivaramakrishna, L., & Reddy, A. V. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *Journal of hazardous materials*, (2012). *203*, 118-127.

[27]. Kumar, B. S. Kinetics, equilibrium, isotherm and thermodynamic modeling of sorption of Reactive Yellow 37 on to balsamodendroncaudatum wood waste activated carbon. *JOURNAL OF ADVANCED APPLIED SCIENTIFIC RESEARCH*, *1*(1), (2015). 97-107

[28]. Singh, K., & Padmesh, T. V. N. Biosorption of Dyes onto Mango Seed and Pineapple Peel. (2014). Retrieved from http://www.taylors.edu.my/EURECA/2014/downloads/56.pdf

[29]. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical society, 40(9), (1918), 1361-1403.

[30]. Freundlich.H, Uber die adsorption in losungen, Zeitschrift Physikalische Chemie (Leipzig), 57A, (1906), pp385-470

[31]. Sohn, S., & Kim, D. Modification of Langmuir isotherm in solution systems—definition and utilization of concentration dependent factor.Chemosphere, (2005). 58(1), 115-123